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by
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described by infra-red methods. It is demonstrated in this report that over a very wide range of densities concordant values for the degree of crystallinity are obtained by infra-red and density methods irrespective of the type of crystallite morphologies that are observed. Moreover, it is shown that the absorption properties at room temperature of the gauche bands in bulk crystallized polyethylene, which are assigned to the noncrystalline regions, are identical to those of the melt of monomeric normal hydrocarbons. Hence, it is concluded that the structure of the noncrystalline regions in polyethylene at room temperature is very similar, if not identical to, that of the pure melt.

The first phase of the study of the radiation chemistry of crosslinking has been concluded. Enough information has been obtained to proceed with the effective preparation of networks. A brief manuscript is being prepared describing the important role of the vinyl end group in causing the more efficient crosslinking in the crystalline state. This conclusion is based on the studies with hydrogenated polyethylene that were described in detail in the last report. The crosslinking efficiency was found to be about the same for crystalline and amorphous samples having the end-group hydrogenated. However, for the same fraction, which contained the vinyl end-group the crosslinking was about twice as effective in the crystalline state. A large amount of data involving the kinetics of the various radiochemical acts has been collected. These are now being analyzed with the purpose of developing a quantitative mechanism for crosslinking.

With the conformation that has been developed in regard to crosslinking effectiveness highly oriented and highly crystalline samples of polyethylene are now being prepared in order to study the properties of the networks formed.

These include highly oriented fibers, and fibers formed by crystallization from dilute solution in a hydrodynamic shear field. A large amount of preliminary study is required in the latter system in order to describe the orientation and crystalline state. This work is currently in progress. In addition it is planned to study networks formed from highly crystalline polymers which will require low molecular weights. The major interest is on the effect of crosslinking on the melting temperature and entropy of fusion and properties of the melt.

Studies are continuing on the broadline nuclear magnetic resonance spectra of molecular weight fractions of polyethylene to develop more of an understanding of the molecular motions in the crystalline and amorphous regions. Some difficulties with the spectrometer, in studying the highly crystalline samples, have been encountered. It is expected that these difficulties will be alleviated in the near future.

The major areas of research in this program are concerned with the fundamental acts of crosslinking polymers by means of high energy radiation and the dependence of the crosslinking efficiency and resultant network properties on the state and temperature of the system at the time the crosslinks are introduced. The main experimental investigations have been with molecular weight fractions of polyethylene. The very early results that were obtained in the initial phases of the progress made clear that the crosslinking process depends not only on a distinction between the crystalline and amorphous state but also on the type of crystallite morphology present. In addition, it was shown that temperature must be considered as an independent variable and has its own independent influence on the crosslinking efficiency besides altering the crystalline-amorphous ratio. Because of these general conclusions it became necessary to examine in some detail the chemical acts involved in radiation crosslinking and to study some aspects of crystallite morphology.

Manuscripts describing work supported by this grant that have appeared in press since the last report are:

(1) T. Okada and L. Mandelkern, "Effect of Temperature, Phase and Molecular Weight on the Irradiation of Linear Polyethylene: I. Irradiation in the Completely Molten State", Proceeding of the International Symposium on Macromolecular Chemistry, Japan 1966.

(2) T. Okada and L. Mandelkern, "The Infra-red Determination of the Degree of Crystallinity of Polyethylene Crystallized from Dilute Solution", J. Poly. Sci. 4B, 1043 (1966).

A manuscript "The Effect of Morphology and Degree of Crystallinity on the Infra-red Absorption Spectra of Polyethylene" by T. Okada and L. Mandelkern is in press in the Journal of Polymer Science and is scheduled to appear shortly. This paper is a very detailed account of how polyethylene can be